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U.S. ENVIRONMENTAL PROTECTION AGENCY

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STUDIES OF SMALL PARTICLES

IN SOLID WASTE OPERATIONS

A Solid Waste Research
Open-File Progress Report (RS-03-69-39)

written by
NANCY S. ULMER, Research Chemist

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Monitoring
Solid Waste Research
1971

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ABSTRACT

The installation of a Small Particle Studies Laboratory and the familiarization with the principles, techniques, and instrumentation of industrial microscopy and Coulter Counter technology are described. The development evaluation, and utilization of procedures for preparing a library of solid waste samples, permanent sample mounts, and photomicrographs are reviewed. A tentative classification or identification of typical particles in six solid waste samples is reported. The need for developing and perfecting analytical expertise in the isolation, concentration, and orientation of solid waste particles before attempting to confirm their tentative classifications or identifications by determining their physical, chemical, and optical properties is stressed. Additional investigations, designed to develop and evaluate procedures for determining the particle size distribution of incinerator fly ash samples and for identifying and estimating specific components of particular significance in the management or recovery of solid wastes are proposed.

INTRODUCTION

The Resource Recovery Act (Sec. 101), recently enacted by Congress, provides for the promotion, development, evaluation, and application of solid waste management and resource recovery systems which preserve and enhance the quality of our air, water, and land resources.[1] To facilitate the attainment of this goal, the Act (Sec. 103) also provides for the conduct of investigations and surveys of the identity of solid waste components and potential materials and energy recoverable from solid wastes.

In the past, chemists charged with the responsibility of characterizing solid wastes and related samples, have usually employed volumetric, gravimetric, spectrophotometric, and atomic absorption techniques to detect and measure the ions, elements, and occasionally the organic groups present in the samples. Industrial, pharmaceutical, and forensic chemists have recently demonstrated, however, that (1) the size distribution of particulate samples can be determined using the Coulter Counter and (2) the identity, form, and source of both the elements and the compounds present in particulate samples can be determined using the microscope and related instrumentation. An investigation was, therefore, initiated in the Research Services Laboratory to evaluate the applicability of the techniques of industrial microscopy and Coulter Counter technology in the characterization of solid waste particles collected from the environs within or adjacent to solid waste processing sites.

GENERAL APPROACH

An extensive review of existing techniques for the determination of the

size distribution and microscopic identification of small particles was first performed to permit the formulation of a general scheme for the characterization of solid waste particles. When sufficient permanent laboratory space became available, the previously purchased Coulter Counter, microscopes, cameras, and related equipment was assembled, installed, briefly evaluated, and modified when necessary. Approximately 150 solid wastes and 100 plastic samples were then secured for use in the development and evaluation of procedures for determining the identity and size distribution of solid waste particles.

Research endeavors, to date, have included (1) the preparation of reference samples, sample mounts, and photomicrographs of typical solid waste particles, (2) the detection of the solid waste components which can be easily classified and/or identified by their morphological, physical, chemical, and optical properties, (3) a preliminary evaluation of the applicability of a tentative Coulter Counter technique for determining the particle-size distribution of fly ash particles, and (4) the proposal and consideration of specific, significant solid waste particle components whose identification and estimation might be effected or supplemented by the techniques of industrial microscopy and Coulter Counter technology after additional research has been performed.

EXPERIMENTAL APPROACH AND RESULTS

Familiarization with Industrial Microscopy and Coulter Counter Technology

An extensive literature review of the textbooks, journal articles, and movies published by and for the optical mineralogist, resinographer, and

chemical microscopist was first performed to familiarize the analyst with the basic principles, techniques, and types of instrumentation for determining the morphological, physical, chemical and optical properties of particulates. Attendance at the U.S. Public Health Service's Training Course, "Air Pollution Microscopy," provided practical instruction and experience in the collection and mounting of air particulates and in the determination of the size, crystal form, refractive indices, and extinction of known compounds. Attendance at two conventions, Inter-Micro 70 and the Coulter Counter User's Conference, along with personal conferences with experienced analysts such as Donald Grabar (American Cyanamid, Stamford, Connecticut), Shepherd Kinsman (Coulter Electronics, Hileah, Florida), Dr. Walter McCrone (McCrone Associates, Chicago), Dr. Theodore Rockow (Dept. of Textile Technology, North Carolina State University), and Dr. Harvey Sunderman (Dept. of Geology, University of Cincinnati) provided additional knowledge of the performance and applicability of the techniques of thermal and optical microscopy and Coulter Counter technology. A general scheme for particulate analyses was then proposed and adopted (See Figure 1).

Installation, Evaluation, and Modification of the Laboratory Equipment

In the Autumn of 1970 the Orthoplan Research Microscope, the Ortholux Polarizing Microscope, the tungsten, xenon, and monochromatic light systems, the micromanipulator, the microspectrophotometer, the Aristophot and Orthomat Cameras, and the Coulter Counter and related instrumentation were moved to the new Small Particle Studies Laboratory (Room 404). The assembly and installation of, and familiarization with the instrumentation was accomplished using the verbal or written instructions provided either by the respective instru-

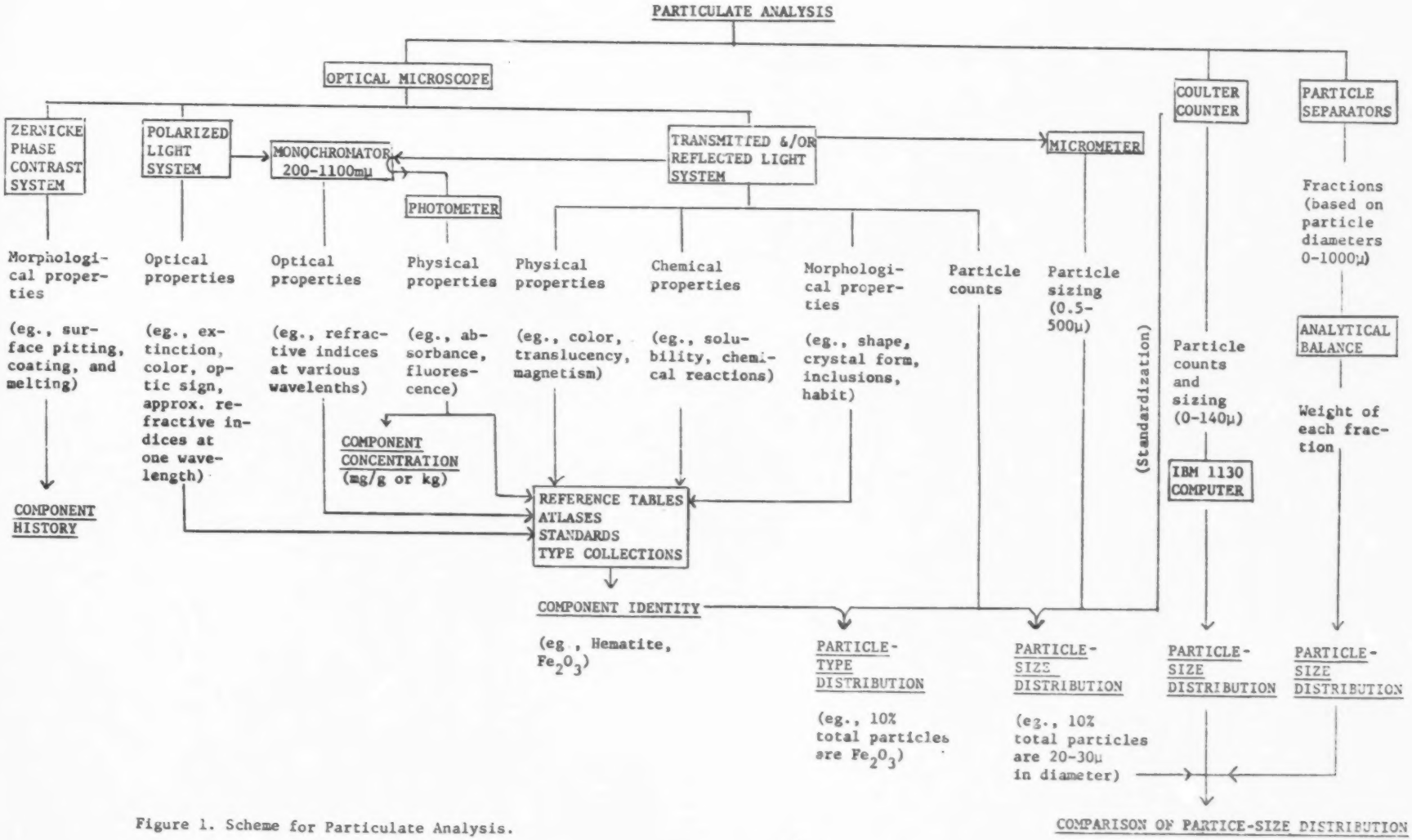

Figure 1. Scheme for Particulate Analysis.

ment manufacturers or other microscopists.

When the initial investigations revealed that certain installation and operating instructions were inapplicable, the following modifications were suggested, developed, requisitioned and/or performed:

(1) Introduction of a spacer into the tube of the polarizing microscope to permit the elevation of the objective nosepiece, objective stage, and condenser lens and introduction of the monochromatic light system , required for the determination of the refractive indices of particles;

(2) Alteration of the dimensions of the microscope bench or support to permit the analyst to be seated while using the polarizing microscope;

(3) Conversion of the Coulter Counter manometer to permit the counting of particles whose diameters range up to 140μ;

(4) Elimination of the exposure "guesswork" and introduction of the use of the Micro-Six Exposure Meter in the preparation of Polaroid photomicrographs with the Aristophot Camera (No meter is normally supplied with the camera).

(5) Use of the next lower ASA setting and a DH (darkfield-brightfield) mid-point setting of "70%" on the automatic exposure control of the Orthomat Camera during the exposure of High-speed Ektachrome and Kodacolor films (ASA seetings of 160 and 80 are not possible on the Orthomat control).

Establishment of a Library of Reference Materials

Sample Preparation

A refuse or compost sample was dried in a mechanically convected or forced-air oven at 70 C while a residue or fly ash sample was dried at 105 C. The diameters of the solid waste particles were then reduced to 2 mm (or less) using a Wiley mill. After the sample's components were mixed on a 14-rpm rotating wheel for 30 minutes, they were redried at the aforementioned temperature. A 1- to 3-g subsample of each pepared solid waste was then stored in a labelled, tightly capped, 5-ml vial. As each vial was added to the sample library, a record of the sample number, type, source, and method of collection and preparation was added to the sample log.

The four plastic samples, employed in the initial studies, were each ground separately in the Wiley mill using a 2-mm sieve. Since the particles became charged and adherred to the upper portion of the mill, the grinding process had to be interrupted frequently in order to brush the particles back down onto the knife blades. Consequently, some contamination of the sample with the brush bristles and dust occurred. As the grinding of each plastic sample was completed, a 1- to 3-g subsample was transferred to a 5-ml vial. The capping, labelling, and storage of the vial and the sample log entry were accomplished as previously described.

Sample Mount Preparation

Several permanent sample mounts of a refuse were first prepared by (1) placing 0.5 to 1.5 mg of a sample on a clean, scratch-free, colorless

microscope slide (75x25 mm), (2) adding 3 to 5 drops of the mounting fluid, Arochlor 5442 (obtained from Monsanto Chemical Company and gently heated to 85 C on a hot plate), (3) gently lowering a round coverslip (18 mm in diameter, 0.16 to 0.19 mm in thickness) at an angle over the immersed particles, (4) then removing any excess cooled mounting fluid with a swab dipped in benzene or ethyl alcohol. Use of this technique resulted, however, in the entrapment of a great number of air bubbles under the coverslip. An evaluation of several procedural variations revealed that the number of bubbles might be decreased by pre-warming the slide on the 85-C hot plate surface, and allowing the mounting fluid to flow under the edge of the coverslip, previously lowered at an angle over the dry (non-immersed) particles. This modified procedure was then employed in the preparation of duplicate permanent mounts of the following samples: four solid wastes from Delaware County, Pennsylvania--namely, a refuse (RSL 69-102), the combustible and fines fractions of an incinerator residue (RSL 69-113 and 69-112, respectively), and an incinerator fly ash (RSL 69-93); two composts-- one from Johnson City, Tennessee and the other from Germany; Cincinnati Enquirer newspaper fragments; and four plastics--polyethylene, polypropylene, polysytrene, and polyvinyl chloride.

During the mounting of each of the four plastic samples, a change in the color and/or shape of the plastics was observed immediately after their contact with the mounting fluid. Since plastic investigations, performed elsewhere, have indicated that most plastic samples are affected by the temperature and/or chemical action of the majority of mounting fluids,[2] the preparation of permanent mounts of plastics was discontinued.

When reference examinations are required, several particles can be removed from the storage vial and examined either directly on a slide or immediately after their immersion in a refractive index fluid.

Photomicrograph Preparation

Each sample mount was examined microscopically and typical solid waste particles selected for photomicrography. A rectangular-coordinate grid pattern, composed of 1-mm squares, 0.1-mm graduations, and numbers and letters for easy area identification (e.g., Lovins Field Finder, available from R. P. Cargille Laboratories, Cedar Grove, New Jersey), was successfully employed to code the location of the selected particles on the sample mount.

The photomicrographs were prepared using (1) the Orthoplan Research Microscope with properly adjusted brightfield-transmitted, polarized-transmitted, incident, or polarized-incident light; (2) the Aristophot (4x5 inch) Camera with the Micro-Six Exposure Meter or the Orthomat (35 mm) Camera with the previosuly suggested exposure control settings; and (3) Polaroid film types 58 and 55 P/N or Eastman film types CX 135 (Kodacolor) and EH 135 (High-speed Ektachrome). As each exposure was made, the following data was recorded in a photomicrograph log: the number of the photomicrograph, sample, and sample mount; the source and identity of the sample; the location of the photographed particle(s) on the sample mount; the type of microscope, tube, objective lens, tube eyepiece, condenser lenses, filters, and aperture setting; the type of illumination; the type, source, and control (transformer setting) of the light; the type of camera and camera lens; the

use and extension length of a camera bellows; the magnification of the objective, eyepiece, tube, and camera lenses and the image on the prepared negative and/or print; the film type, speed (ASA rating), packet or roll number, and expiration date; the exposure meter readings or exposure control settings; the length of the exposure and development periods; and any other pertinent observations. The instantaneous processing of the Polaroid films and the special chemical treatment, required for the preservation of Polaroid prints and type 55 P/N negatives, was performed in the laboratory, but the Eastman films were developed and printed by commercial processing laboratories. The photo number and sample identity were written on the back or margin of each photomicrograph.

The magnification of the photomicrographic image was calculated using the magnification (or reduction) factor of the objective, tube, eyepiece, and camera lenses, the print enlargement factor, and (in the case of the Polaroid prints) the ratio of the length of Aristophot bellows extension to the normal distance of vision (25.6 cm). The magnification was then recorded on the photomicrograph and in the photo log. Since it appears that the exact enlargement of 3R prints, prepared from 35-mm negatives may vary with the processing laboratory, it is recommended that the appropriate magnification scale be experimentally determined in the future and then placed directly on the photomicrographic prints.

Periodically the quality of the photomicrographs was evaluated and appropriate modifications in technique or instrumentation made when necessary. Forty Polaroid and Kodacolor photomicrographs, displaying the morphological characteristics of typical solid waste particles were selected and mounted with appropriate descriptions in an album. Preparation of additional Koda-

color negatives and prints of the solid waste particles will permit the preparation of duplicate albums if required in the future.

Photographic experiments revealed that the orientation of the microscope image on the film can be varied in the Orthomat Camera by rotating the camera about the axis of the microscope tube. The framing and focusing of the image on the film plane can then be accomplished using a similarly rotated graticule, located in the microscope eyepiece. In the Aristophot Camera system, the orientation of the microscope image on the film plane is limited to the orientation of the sample mount of the microscope stage. The framing and focusing, moreover, have to be performed at the screen level, where the magnitude of the light is less than that observed in the microscope eyepiece. It was also observed that the framing guidelines on the Aristophot screen are offset approximately 0.25 inch.

Additional studies revealed that the color, depth, contrast, and sharpness of the photomicrographic images can be improved using (1) a temperature conversion filter and a polarizing filter in the illumination; (2) the minimum condenser aperture diameter, and (3) a high-magnification plano objective in conjunction with a low-magnification eyepiece and/or camera lens.

The average Micro-Six Exposure Meter readings of the particle images, reflected on the Aristophot screen, provided excellent guidance in the exposure of Polaroid film to the brightfield microscope images. The film exposures, required for some darkfield images (i.e., images produced with polarized and/or incident light) had to be determined experimentally, however, since the amount of light reflected from the Aristophot film plane onto the screen was below the minimum detection level of the exposure

meter. Similarly, the previously suggested modifications in the exposure control settings for the Orthomat Camera appeared applicable in the preparation of Kodacolor negatives and High-speed Ektachrome transparencies of the brightfield images. Since the control settings yielded over-exposures of some of the darkfield images, the use of other ASA and DH (darkfield-brightfield) settings must be considered.

The applicability of five films in the preparation of photomicrographs was determined by evaluating the cost and/or quality of the photomicrographs. Inquiry quickly revealed that Ektacolor-L (4x5 inch) prints were very expensive (See Table 1) and hence inapplicable for general use. Although color and black and white photographic prints could be quickly obtained with Polaroid film types 58 and 55 P/N, the use of these films was discontinued after observing that the prints were characterized by a moderately high cost, a lack of exposure reproducibility, inferior color balance, and poor contrast. The latter was particularly evident in the black and white photomicrographs of solid waste particles illuminated by incident and polarized-incident light (i.e., darkfield). The development and/or printing of the Kodak film types EH 135 and CX 135 by commercial laboratories was time-consuming but yielded photomicrographs characterized by a low cost, greater reproducibility, and better color balance, definition, and contrast. The use of these two films for the preparation of additional color photomicrographs for the reference library was recommended. When additional inquiry revealed that the sharpness and contrast of the inexpensive Kodak Plus-X Pan black and white prints were superior to that of the black and white prints, prepared directly from Kodacolor (CX 135) negatives, the use of Plus-X Pan film was recommended for the preparation of negatives

TABLE 1

A COMPARISON OF THE COST OF PHOTOMICROGRAPHS

Film			Products		Cost (in Dollars)/photomicrograph				
								Total	
Type	Identity	Size	Intermediate	Final	Film	Develop-ment	Printing*	First Product	Add'l Product
Black and white	Kodak Plus-X Pan	35 mm	Negative	Print	.04	.04	.15	.23	.15
Black and white	Polaroid, type 55 P/N	4x5 inches	Negative	Print	.50	.05†	---	.50	.15
Color	Ektachrome-EH (High-Speed)	35 mm	-------	Positive transparency‡	.08	.07	---	.15	.30
	"	"	-------	Print§	---	---	---	---	.32
Color	Ektacolor-L	4x5 inches	Negative	Print	.68	.75	3.00	4.43	3.00
Color	Kodacolor-CX	35 mm	Negative	Print	.08	.04	.25	.37	.25
Color	Polacolor, type 58	4x5 inches	--------	Print	1.02	---	---	1.02	---

* The printing costs are based on the preparation of 3R (3 1/2 x 5-inch) prints from 35-mm negatives and 8 x 10-inch prints from 4 x 5-inch negatives.

† This cost is applicable only when additional prints are required.

‡ The transparency is mounted and can be projected.

§ A Kodacolor print can be made directly from the transparency.

and prints for publication.

General Evaluation of Microscopic Techniques for Classifying and Identifying Solid Waste Particles

Morphological Examinations

Duplicate mounts of the six aforementioned solid waste samples were examined using the properly adjusted brightfield-transmitted, polarized-transmitted, incident, and polarized-incident light. A simple coding of the shape, color, and transparency of some of the particles was performed using part of the six-digit coding system recommended by McCrone, et al.[3] Since the sampl mounts were part of a permanent library collection and the particle orientations had to be preserved for preparation and comparison of additional photomicrographs, the isolation and reorientation of the individual particles, as required for the determination of some of their optical properties and hence their complete coding or classification, was not performed. A comparison of the general morphology of the particles with the morphology of the photomicrographic images, published by McCrone et al.,[4] did enable the analyst to make, however, a tentative classification or identification of (1) paper and vegetable fibers, wood particles, stellate hairs, spores, and/or glass in refuse, compost, and the combustible fraction of incinerator residue; and (2) unburned materials (wood, textiles, garbage, and paper) and the unfused and fused ash in incinerator residue and fly ash samples.

The initial morphological examinations of the duplicate refuse, residue, and fly ash samples also revealed a variance in the types and total numbers of particles occurring in the mounts. Evidently each 0.5- to 1.5-mg

subsample, mounted on a microscope slide, is not representative of the solid waste received by the laboratory for analysis. In addition, the estimated average number of glass particles, observed in the mounts, appeared suprisingly low. A brief review of the history and development of sample preparation techniques indicated that the methods currently used in this laboratory, have not been designed to reduce the particle diameter of non-combustibles (glass, metals, ceramics, and rocks). Most of the non-combustibles are, therefore, usually removed from the samples prior to their shipment to and preparation in the laboratory. Precise and accurate qualitative and quantitative microscopic analyses of the total solid waste sample, collected at a processing site, or of a partial sample, prepared by fractionation, can not be performed until additional sample preparation procedures are developed and evaluated.

Physical, Chemical, and Optical Examinations

The complete determination of the six-digit classification and the confirmation of the tentative identification of the solid waste particles can be accomplished after determining some of the following physical, chemical, or optical properties: density, magnetism, melting point, solubility, chemical reactions, refractive indices, birefringence, pleochroism, extinction, and dispersion staining. Since the determinations of these properties are performed with greater ease and accuracy on isolated, concentrated, and/or properly orientated particles, the analyst has proposed the use of a magnet, density fluids, and a density-gradient column for the isolation and concentration of particles. Analytical expertise in the operation of the micromanipulator and the orientation of particles must also

be developed. Since some isolated particles might best be identified after determining just their dispersion staining or chemical reactions, a special dispersion-staining objective with annular and central stops and appropriate identifying chemicals have recently been secured. The applicability and purchase of a microscope hot stage is also being considered. It is anticipated that the development of expertise in determining and correlating the physical, chemical, and optical properties will eventually enable the analyst to classify and identify solid waste particles by performing a minimum number of determinations.

General Evaluation of a Coulter Counter Technique for Determining Particle-Size Distribution of Solid Wastes

Sample Preparation and Preliminary Analyses

Fly ash particles, collected on six fiberglas filters by the Processing staff of Solid Waste Research, were used to evaluate the applicability of a tentative Coulter Counter technique for determining particle-size distribution. Each predried filter was first placed in a covered petri dish and the unit weighed. The particles were then rinsed from the filter by gently flowing deionized water across the filter surface. The resulting suspension was rinsed from the petri dish to a sieve system. The petri dish, containing the filter, was dried in a 70-C oven, cooled to room temperature in a desiccator, and then reweighed. The weight of the particles, removed from the filter, was calculated and recorded.

The sieve system, employed in this preliminary fractionation, consisted of a receiver and four preweighed sieves whose stainless steel mesh openings were 125, 105, 47, and 12 μ in size. The fractionation was accomplished using

additional small quantities of deionized water. The final filtrate, containing particles 12 μ (or less) in diameter, was washed from the receiver into a previously weighed 100-ml beaker. After drying each fraction in a 70-C oven and then cooling it to room temperature in a desiccator, the final weight of each sieve and beaker was determined. The weight of each fraction and the percent by weight of each fraction were then calculated.

Although these initial studies revealed that the brass sieve holders and receivers tended to decompose (and hence contaminate the fractions) after repeated exposure to aqueous suspensions of fly ash particles, inquiry has indicated that the use of stainless steel or rhodium-plated sieve holders and receivers should permit accurate and precise fractionations in the future.

The final phase of the sample preparation was effected by suspending each fraction of the four non-contaminated samples in 4 percent sodium pyrophosphate, which had been freshly prepared and filtered four times using a stainless steel Millipore® system equipped with Solvinert™ filters, having a pore size of 0.25 μ.

Analyses with the Coulter Counter Model B

Since 86 percent (or more) of the particles in the four samples were less than 12 μ in diameter, a particle-size distribution of just this fraction of each sample was requested. The preliminary evaluation of the Coulter Counter technique was, therefore, limited to the use of a 30-μ aperture tube and the electrolyte, 4 percent sodium pyrophosphate.

The directions, provided in the instrument manual,[5] were generally employed to set up and maintain the Model B Coulter Counter with the 30-μ

aperture tube. The mercury, chemically cleaned with 10 percent nitric acid, was also filtered several times through a Type "G" Mercury Filter (obtained from Bethlehem Apparatus Co., Inc., Hellertown, Pennsylvania) before its introduction into the manometer. The sodium pyrophosphate solution was originally stored in brown glass bottles. When the formation of small crystals (probably due to the leaching of calcium from the glass and the formation of calcium phosphate) was observed in time, storage of the solution in plastic bottles was initiated. The cleaning of the aperture tube was usually accomplished using a detergent solution and a small test tube brush, but occasionally it was advantageous to soak the tube in a sulfuric acid-dichromate cleaning solution for several hours. After thorough rinsing with water, the tube was then soaked in a solution of Triton X-100 (McKesson Chemical Co., Evendale, Ohio) for a similar period and rinsed again. The Triton X-100 solution is a wetting agent and was employed in an effort to minimize the adherence of air bubbles to the aperture tube during its use in an analysis. Evacuation of the air from the electrolyte solution, just prior to its introduction into the reservoir and sample beakers, also appeared to minimize the occurrence of bubbles in the aperture tube during its initial filling with the electrolyte solution.

The calibration of the specified system was also performed as directed in the manual. Since a 100,000-ohm-per-volt-voltmeter was not available, the resistance of the electrode-electrolyte-tube system could not be accurately determined in our laboratory. When a member of the Coulter Electronics Laboratory staff indicated that the resistance of this system usually is between 30,000 and 50,000 ohms,[6] the matching switch position,

"32H", was selected. Latex particles, 1.947 μ in diameter, (obtained from Coulter Diagnostics, Inc., Miami Springs, Florida) were then suspended in 200 ml freshly filtered 4 percent sodium pyrophosphate. After gentle mixing was accomplished with the stirring assembly, "k", the calibration factor was determined using the 30-μ aperture tube and gain, current, and amplification switch settings of 50, 1, and 1/2, respectively.

In preparation for the analyses of the four fly ash samples, a determination of the size distribution of particles in a blank sample (i.e., filtered electrolyte) was performed. As the threshold, aperture current, and amplification settings were altered to permit the counting of particles, less than 3 μ in diameter, it was immediately noted, however, that interferences in the oscilloscope pattern and the magnitude and variability of the counts were all increasing with each decrease in particle size. Some of the interferences appeared to be 30-cycle and/or 60-cycle in nature, while others seemed more erratic and spasmatic.

To minimize the possibility of interference from electric line noise, the instrument was transferred to its own 110-v power line and a borrowed Sola constant voltage transformer and capacitor introduced into the line. Since the stirring motor and microscope light were not grounded (i.e., only a two-wire cord had been provided for each accessory by the manufacturer), a ground wire was attached to the stirring motor assembly and run to the light, and thence to the base of the manometer stand, and finally to a nearby water pipe. An on-off switch was also installed in both the stirring motor and vacuum pump lines to permit the cessation of the stirring and vacuum activities during the counting of particles, 3 μ (or less) in diameter. Lastly, the neon light on the manometer stand was disconnected and a voltage

loss in the stirring motor electric plug corrected. Although these efforts greatly reduced the interferences due to line-voltage variations and inadequate grounding, a slight 60-cycle interference persisted on the oscilloscope at the aperture current and amplification settings, employed to count particles, 1 μ (or less) in diameter.

Persistent investigation of the erratic and spasmatic interferences, observed on the oscilloscope, eventually indicated that they were caused by vibration and/or radiation noises from nearby instruments, such as electric typewriters, computers, centrifuges (with brushes), vibrating air-conditioning units and a sterilizer. Even the heel clicks of a few persons, frequenting the nearby hall, were registered on the oscilloscope and counted as particles. The installation of three rubber typewriter pads under the entire instrument and the envelopment of the manometer stand in an aluminum foil "cocoon", clamped to the base of the manometer stand and also attached to the extra ground wire, did not eliminate these interferences. A decided reduction in radiation and vibration interferences was recently observed, however, when a blank analysis was performed after the cessation of activities in the nearby offices and laboratories at the end of the day. It is, therefore, recommended that a vibration-, radiation-, and sound-proof shield be constructed around the instrument, particularly the manometer stand, before any additional analyses of samples be attempted. Although the cost of the rubber, acoustical tile, and metal mesh or screening, required for the enclosure, may exceed $100, the shield should reduce the interferences and ensure the accuracy and precision of future analyses.

Analyses with the Coulter Counter Model T

In an effort to fulfill the complete analytical request of the Processing staff without further delay, the four suspensions, containing particles, 12 μ (or less) in diameter, were transported to the Fairfax Facility. In the Research Laboratory of the Office of Air Pollution the particle-size distribution of each suspension was determined using the Coulter Counter technique, 4 percent sodium pyrophosphate as the electrolyte, the 30-μ aperture tube, and a recently purchased Coulter Counter Model T. The latter, situated on a very stable and well-shielded bench, was calibrated and operated according to the directions in the instruction manual.[7]

During the course of the four analyses it was observed that the new model is capable of (1) performing simultaneously a single determination of the population of particles exceeding each of 14 particle diameters (the smallest being 0.595 μ); (2) computing the cumulative populations, the relative differential volumes, and the cumulative relative volumes; and (3) printing out all the data within a few minutes. Since the calculation of the particle-size distribution from the cumulative relative volumes requires only a few additional minutes with a desk calculator, the total time required to complete a determination is 5 to 10 minutes and quadruplicate determinations approximately 30 minutes. The performance of (1) quadruplicate estimations of particle populations at each of 14 sets of switch positions on the Coulter Counter Model B and (2) all the desk calculator-type computations required for determining the particle-size distribution would require a 4- to 5-hour effort. Although the cost ($18,000) of the Coulter Counter Model T far exceeds that of our Model B or the new transistorized Model B, it is evident that the Model T is the model of choice when the number of man-hours expended per analyses must be considered.

Proposed Particle Characterization Studies

The FY 71 investigations were designed to provide the analyst with an opportunity to develop analytical expertise and initiate the evaluation of the applicability of microscopic and Coulter Counter techniques in the general characterization of solid waste particulates. The following investigations, proposed for future initiation, should afford an evaluation of the applicability of these techniques in the classification, identification, and estimation of specific particles of particular significance in the management and recovery of solid wastes.

Classification and Identification of Specific Solid Waste Components

Carbonates. Recent Research Services Laboratory analyses of incinerator residue and fly ash samples have demonstrated the presence of up to 7.91 percent carbonate carbon or 39.05 percent carbonate.[8] Since the common carbonate compounds decompose at different temperatures (Table 2), the microscopic detection and identification of the specific carbonate compound(s) may provide an estimate of the actual solid waste temperature achieved during the incineration and hence an additional evaluation of the quality of the residue and fly ash and the efficiency of the particular process and/or incinerator.

A review of the published morphological, physical, chemical, and optical properties of carbonates indicates that they can be identified by determining their density, shape, color, transparency, refractive indices, extinction, and/or dispersion-staining. Isolation and concentration of the carbonates may be necessary at first, but the handling and number of determinations, required for identification, should decrease as expertise is gained.

TABLE 2

DECOMPOSITION TEMPERATURE (C) OF CARBONATES

Compound		Decomposition Temperature (C)*
Formula	Common Name	
$Na_2CO_3.H_2O$		35.1
$(NH_2)CO_3.H_2O$		58
$KHCO_3$		100-200
Ag_2CO_3		218
$2CuCO_3.Ca(OH)_2$	Azurite	220
$PbCO_3$	Cerrusite	315
$MgCO_3$	Natural Magnesite	350
$2PbCO_3.Pb(OH)_2$	White Lead	400
$CdCO_3$		<500
$CaCO_3$	Natural Aragonite	825
	Natural Calcite	898.6 †
	Pure Calcite	960 ‡

* Unless otherwise specified, the values were obtained from N.A. Lange, ed. Handbook of Chemistry. New York, McGraw Hill Book Company, 1967. p. 230-349.

† From Robert C. Wuest, ed. Handbook of Chemistry and Physics. 45th ed. Sect. B. Cleveland, The Chemical Rubber Company, 1964. p. 161.

‡ Personal communication. Dr. G. C. Ulmer, Temple University, Philadelphia to Nancy S. Ulmer, Solid Waste Research, March 2, 1971.

Toxic Metallic Components. Atomic absorption analyses, performed in the Research Services Laboratory, have demonstrated the presence of cadmium, mercury, selenium, and zinc in solid wastes.[9] Preliminary air pollution surveys of published investigations of these heavy metals and their compounds have indicated that certain forms of each metal are more toxic than others.[10,11,12,13] If the particular form of each of these (and other) toxic metals, could be identified, scientists and engineers might be able to (1) determine more accurately the real potential hazards, associated with the release of such materials into the environment surrounding a processing or recovery site; (2) develop physical or chemical means of reducing or eliminating the hazard; and (3) evaluate and enhance the efficiency of solid waste management and resource recovery systems in preserving our air, land, and water resources.

Analyses of solid waste and related samples by industrial microscopy techniques should provide identifications of the form (and possible source) of the toxic metallic materials being emitted from incinerator stacks, leached from refuse in land disposal sites or evolving from other processing and recovery sites. A review of the aforementioned solid waste analyses indicated that the concentration of each of the four metals appears to fall within the microgram-to milligram-/gram range. Since 0.5- to 1.5-mg solid waste subsamples are usually mounted on a slide, the total weight of the metal on the slide would probably be in the nanogram-to microgram-/gram range. Although nanogram, (and, occasionally, picogram) quantities of a substance have been studied by experienced optical microscopists, identification of the form(s) of a metal (i.e., element and/or specific compounds) might best be accomplished by first isolating and concentrating them by density techniques (e.g., heavy metals will sink

during centrifugation of suspensions of solid wastes in methylene iodide or aqueous thallium formate-malonate solutions.)

If research indicates that the metal form can not be detected or identified by optical microscopy techniques, then the use of the electron microprobe and/or the electron scanning microscope is suggested. A brief general evaluation of the applicability of either (or both) of the instruments can be effected by contracting a few analyses to a materials science laboratory.* If the analytical results of the contracted research indicate that the instrumentation will permit the identification of the elemental and compound forms of the metal, additional solid waste analyses could then be either contracted or performed in-house after purchasing the necessary instrumentation.

Plastics. A published review of the role of packaging materials in solid waste management reveals that 90 percent of the 51.7 million tons of packaging materials, generated in the United States in 1966, entered the solid waste stream and accounted for 13.3 percent of the total solid wastes.[14] A recent communication of the Bureau of Mines has indicated, moreover, that 74 percent of the plastics in 800 lbs of household plastics, collected in Rolla, Missouri, were polyolefins (polyethylene and polypropylene) while 19 percent were polystyrene; the remaining 7 percent included polyvinyl chloride and other plastics.[15] Although plastics currently represent only a small percentage of the total solid wastes, a 152-percent

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* Dr. Gene White, Materials Science Laboratory, Pennsylvania State University, is currently employing this instrumentation to characterize coal-fired emissions for the Bureau of Mines.

increase in the per capita consumption of plastic packaging materials alone is anticipated by 1977.[16] Perusal of plastic advertisements, moreover, reveals that the plastic industry is continuously developing new plastic formulations or products. The appearance on the market, for example, of an increasing number of plastics displaying resistance to heat or burning is particularly significant.

Since the future development and evaluation of solid waste management or recovery systems may be enhanced by a knowledge of the specific types and identities of plastics occurring in bulk form in the generated wastes or in particulate forms in the processed wastes, the development of techniques for classifying and/or identifying the plastics in solid waste operations is proposed.

An extensive literature search has already revealed that Cobler,[17] Haslam and Willis,[18] Rockow and Gilbert,[19] Roff,[20] and the Modern Plastics Encyclopedia[21] have published or reviewed the schemes, methods, and/or property charts currently employed to classify and identify a plastic (or resin) sample. A study of the published schemes has shown that the analyst must perform morphological, physical, chemical, and optical examinations of subsamples of the plastics before and/or after (1) the physical separation of their constituents or (2) their ignition, fusion, or saponification. The examinations include the determination of many of the following properties: crystallinity, crystal form, phases, color, transparence, density, fluorescence, softening point, spectra, diffraction pattern, solubility, staining reactions, burning properties (flame color, melting, odor, ash production), chemical composition (elemental, group, or simple compound constituents), saponification

and iodine values, refractive indices, and dispersion-staining. A complete analysis, may therefore require the use of not only simple physical and chemical techniques but also the specialized techniques of ultraviolet, visible, infrared, fluorescence, and/or Raman spectroscopy, gas chromatography, and x-ray diffraction and industrial microscopy. Since microscopic and simple, related techniques may provide immediate classification of a plastic, identification of a plastic's constituents, degradation products, and/or derivatives, and a continuous guidance in the design and performance of the complete analysis, the microscope may be considered the hub of the analytical approaches.

The research, proposed for the future, should determine if microscopic and simple related techniques can be employed successfully to detect, isolate, concentrate, classify, and/or identify bulk or particulate solid waste samples containing polyethylene, polypropylene, polystyrene, polyvinyl chloride , and any other plastics of particular significance. The laboratory investigations should include morphological, physical, microchemical and optical examinations of (1) various samples of each of the plastics (i.e., samples obtained from various manufacturers or fabricators), (2) mixtures of samples of various plastics, and (3) solid waste samples before and after additions of mixtures of various plastics.

Determination of Size Distribution of Fly Ash Particles

Previously, the Research Services Laboratory Staff performed, upon request, determinations of the total weight of fly ash particles, collected on a series of filters during the evaluation of the efficiency of a number of incinerators by the Division of Technical Operations Staff. This per-

mitted, of course, only the calculation of the concentration of the particles in the stack emission (i.e., ppm/cu.ft.). Since inhalation of particles, 10 μ (or less) in diameter, may cause lung disease, studies to determine the size distribution of particles on the aforementioned filters (and similar filters, collected in the future) are proposed. Sieve analyses will afford the general separation of the particles, having diameters from 1 to 500 μ, into fractions and thus the determination of the percent weight of each fraction. Coulter Counter analyses will yield a more detailed size distribution of the particles whose diameters range from 1 to 140 μ. The correlation of these results will permit a more complete evaluation of an incinerator's ability to preserve the quality of the environment surrounding it.

CONCLUSIONS

1. The literature and laboratory studies, performed to date, indicate that the principles and techniques of industrial microscopy and Coulter Counter technology can be employed to characterize the components of refuse, compost, incinerator residue, or fly ash samples.
2. Methods for preparing solid waste samples for microscopic analysis must, however, be modified and/or developed to (a) permit the inclusion of non-combustibles in the analyzed samples, (b) minimize contamination from other sources, and (c) ensure the representative nature of not only the sample received and prepared in the laboratory but also the subsample selected for analysis.

3. Permanent reference mounts of refuse, residue, fly ash, and compost can be prepared using the mounting fluid, Arochlor 5442. Plastic particles should just be stored in vials, however, as most mounting fluids affect their morphology.

4. Photomicrographs for publication or reference are best prepared with the Orthomat (35 mm) Camera and the Eastman films, Plus-X Pan (for black and white) and Kodacolor CX 135 or High-speed Ektachrome EH 135 (for color). Additional investigation of the Orthomat Control settings required for exposures of darkfield images, is required.

5. Tentative classifications and/or identifications of (a) paper and vegetable fibers, wood particles, stellate hairs, spores and/or glass particles in refuse and compost and the combustible fraction of incinerator residues and (b) unburned materials and unfused and fused ash in incinerated samples can be made after comparing the morphology (shape, color, transparency) of the unknown particle(s) with the morphology of identified photomicrographic images.

6. Analytical expertise in separating, concentrating or orientating solid waste particles must be developed before attempting to confirm the tentative classifications and/or identifications of particles by physical, chemical, and optical examinations.

7. A 100,000-ohm-per-volt-voltmeter and a special instrument shield should be secured before attempting any additional evaluations or applications of the Coulter Counter Model B in our laboratory. The use of this type of voltmeter will permit the accurate measurement of the resistance of the electrode-electrolyte-aperture tube system and hence ensure the selection of

the most appropriate matching switch position. The shield should reduce the occurrence of radiation, vibration, and acoustical interferences and thus ensure the accuracy and precision of the counts of particles whose diameters are less than 3 μ in diameter.

8. Purchase of a Model T Coulter Counter should be considered if requests for particle-size distribution analyses increase and/or the man-hours expended per analysis must be reduced.

9. Proposed studies of specific solid waste components or samples should provide additional evaluation of the applicability of the techniques of industrial microscopy and Coulter Counter technology in the characterization of small particles in solid waste operations.

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Mention of commercial products or manufacturers in this report does not constitute endorsement by the U.S. Government.

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